**LeS C.7 Health risk - Inorganics**

# THE USE OF $PH_{STAT}$ LEACHING TESTS TO ASSESS CHEMICAL SPECIATION AND POTENTIAL MOBILISATION OF TRACE METALS FROM SOILS, SEDIMENTS AND WASTE MATERIALS: A STATE OF THE ART

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## 1 Introduction

### *1.1 Assessment of pH-dependent leaching behaviour*

pH is one of the key parameters that determines heavy metal mobility in soils and sediments. In many respects leaching behaviour as reflected by the $pH_{stat}$ leaching test and related characterisation leaching tests provide a better means of assessing environmental impact than analysis of total elemental composition (Van der Sloot et al., 1996). A $pH_{stat}$ test allows to assess how the solubility changes if *in situ* pH changes occur. Moreover, information is obtained on the potential buffering capacity of the sample and its sensitivity to pH changes as a result of external stresses (e.g. soil acidification, liming). Different types of test are available to assess pH dependent leaching. In the United States, the TCLP (Toxicity Characteristic Leaching Procedure) is commonly used to determine the toxicity characteristics of a material. The TCLP is a batch test in which the size-reduced material is leached with acetic acid at a L/S ratio of 20 for 18 hours. This test is less suited to estimate metal release over a long period of time, especially since the extraction time for a TCLP is arbitrarily chosen (18 h). Moreover, leaching is addressed at only one pH value.

Although buffer solutions represent a simple way to assess heavy metal mobility as a function of pH (e.g. Tackett et al., 1986), buffer components can induce heavy metal complexation, resulting in unusually high leaching (Gäbler, 1997). Kaupenjohann and Wilcke (1995) presented a $pH_{stat}$ titration in which ion exchange resins were used to remove reaction products. Cation-exchangers provide protons to the suspension while cations are released by pH-buffering of the soil. Manual titrations are rather unpractical and require some knowledge of the acid neutralizing capacity of the sample. Cremer and Obermann (1992) introduced a computer-based titration system allowing continuous registration and fine-tuning of pH during leaching experiments. This system was used by Gäbler et al. (1997) and Paschke et al. (1999), who performed $pH_{stat}$ leaching tests for 24 h. After 24 h, the suspended matter was removed from the liquid phase by centrifugation and filtration. Some standardized leaching test also rely on $pH_{stat}$ titrations. In the German standard leaching experiment (DIN 38 414-4), pH is kept at a preset value (pH 4-11). The L/S ratio is 10 (L/kg) and the duration is 24 hours (Hamer and Karius, 2002). The standardized availability test NEN 7341 (1995) uses $pH_{stat}$ titrations at pH 7 and pH 4. To obtain a larger degree of dissolution, particle size is reduced to < 125 µm and a solid liquid ratio of 1/50 is used. The total extraction time amounts to only 3 hours. The latter test intends to examine the availability for leaching of inorganic compounds in solid materials (waste materials, building materials, soils). The aim is to determine the amount of a component that can leach out of a material upon exposure of the material in aerobic

conditions to extreme conditions (e.g. disintegration of the material or complete consumption of ANC). This test has been criticized for not promoting complete dissolution or equilibrium. Since only the final leachate is analysed and because of the short duration of the availability test, slow buffering reactions are not taken into account. The pH dependence leaching test (PrEN 14429), which has been developed by the Network for the Harmonisation of Leaching/Extraction Tests (SMT-CT96-2066) consists of parallel extractions of the material at an L/S=10 (L/kg) for 48 h at a series of pre-set pH values. In addition, the test provides a measure of acid-base neutralization capacity (ANC/BNC). The most important difference between the above mentioned $pH_{stat}$ tests and the $pH_{stat}$ test used in our laboratory (see also Van Herreweghe et al., 2002), is the longer duration of the test (96 h) and the monitoring of metal release during test. Additionally, the $pH_{stat}$ leaching test was further optimised by adapting the concentration of the titration agent and by adjusting the interval of pH acquisition (see Cappuyns et al., 2004a).


**Figure 1: $pH_{stat}$ multititrator**

### *1.2 Application of $pH_{stat}$ leaching tests*

During the last few decades, $pH_{stat}$ leaching tests have been applied to assess the pH-dependent leaching behaviour of heavy metals in soils (Kaupenjohann and Wilcke, 1995), industrially contaminated sites (Van Herreweghe et al., 2002), waste materials (Ganne et al., 2005), dredged sediments (Cappuyns et al., 2004a, b), overbank sediments (Gabler, 1997; Cappuyns and Swennen 2004) and anoxic river sediments (Cappuyns et al., 2005). Furthermore, $pH_{stat}$ leaching tests have been evaluated as a tool to measure the weathering rates in soils (van Grinsven and van Riemsdijk, 1992). $pH_{stat}$ experiments are less suited to directly estimate weathering rates in soils since the continuous abrasion of mineral particles during stirring or shaking cause an overestimation of weathering rates van (van Grinsven and van Riemsdijk, 1992). In the nineties, the CEN (Comité Eurpéen de Normalisation) started with the harmonisation of new European leaching tests, partly based on existing leaching tests. One of these tests is the $pH_{stat}$ test, which is used

for the characterisation of waste materials and building materials. Although $pH_{stat}$ leaching tests have mostly been applied to study the leaching of heavy metals, Hirner et al. (1991) used $pH_{stat}$ leaching tests to study the leaching behaviour of organic contaminants. Besides for soils, sediments and waste materials, $pH_{stat}$ leaching tests are also frequently used in medical research, for example to simulate the conditions in the digestive tract.

This papers discusses the use and the possibilities of $pH_{stat}$ leaching tests as a tool to assess the potential mobilisation of heavy metals from contaminated soils, sediments and waste materials.

## 2 Materials and methods

### *2.1 Samples*

3 sediment samples with different physico-chemical characteristics and 1 waste material were selected for analysis. Sample GB(dr) is a dredged sediment, disposed on land more than 12 years ago. Samples GB(fo) and GB(cl) were sampled in a regularly inundated floodplain. Sample GB(cl) is a green clay-rich sediment, sampled in the upper part (0-20 cm) of a overbank profile at a distance of 20 m from a river. Sample GB(fo) was taken from the same overbank profile, between 20 and 35 cm depth. This sample was characterised by red-brown and black colours because of the abundant occurrence of Fe-oxides and organic matter. Sample AN(t) is a sample from a tailing composed of waste from the metallurgical process of zinc production. All the samples were oxidised at the moment of sampling. A detailed description of the methods used for the physico-chemical and mineralogical sample characterisation can be found in Cappuyns et al. (2004a) and Ganne et al. (2005).

**Table 1 Physico-chemical and mineralogical characteristics of samples GB(dr), GB(fo), GB(cl) (mean ± standard deviation of 3 replicates) and AN(t). Q=quartz, gl=glauconite, am=amorphous**

| | **Zn** | **Ni** | **Cd** | **Cu** | **As** | **Mn** | **Fe** |
|---|---|---|---|---|---|---|---|
| | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | % |
| GB(dr) | 4083 ± 345 | 84 ± 6 | 213 ± 16 | 182 ± 11 | 254 ± 25 | 527 ± 17 | 8,2 ± 1,0 |
| GB(fo) | 320 ± 13 | 36 ± 2 | 40 ± 2 | 11 ± 1 | 196 ± 4 | 122 ± 6 | 14,7 ± 0,5 |
| GB(cl) | 545 ± 12 | 20 ± 0,5 | 11 ± 0,4 | 26 ± 1 | 103 ± 2 | 64 ± 2 | 11,9 ± 0,6 |
| AN(t) | 30900 | 104 | 124 | 1704 | 1928 | 1468 | 23,1 |

| | **Ca** | **pH ($H_2O$)** | **Org C** | **CEC** | **clay** | **silt** | **sand** | **mineralogy** |
|---|---|---|---|---|---|---|---|---|
| | % | % | % | cmol/kg | % | % | % | |
| GB(dr) | 1,67 ± 0,17 | 6,8 ± 0,1 | 13 ± 1,0 | 19 ± 0,5 | 45 | 42 | 13 | Q, gl, am. Fe-hydroxides |
| GB(fo) | 0,51 ± 0,03 | 6,3 ± 0,1 | 50 ± 1,0 | 31 ± 0,6 | 21 | 29 | 50 | Q, gl, hematite, pyrrhotite |
| GB(cl) | 0,26 ± 0,04 | 6,4 ± 0,1 | 4 ± 0,4 | 33 ± 0,6 | 81 | 15 | 4 | Q, gl, illite, smectite |
| AN(t) | 2,3 | 8,0 | **mineralogy**: troilite, arsenopyrite, willemite, magnesioferrite | | | | | |

### *2.2 $pH_{stat}$ leaching*

The $pH_{stat}$ experiments were carried out with an automatic multititration system (Titro-Wico Multititrator, Wittenfield and Cornelius, Bochum, Germany). 80 g of sediment (< 2 mm fraction) was put in an Erlenmeyer flask together with 800 mL of distilled water and placed on a horizontal shaking device. A pH-electrode and an automatic titration dispenser were attached to each flask. The suspensions were first shaken for 30 minutes without addition of acid and then the titration was started. Previous experiments performed in our laboratory (Van Herreweghe et al., 2002) demonstrated that the rapid addition of acid to the soil-water suspension could lead to an exceeding of the set-point pH. Therefore, the concentration of the titration solution was adapted to the set-point pH (pH 2: 2.5 M, pH 4: 1 M and pH 6: 0.25 M). The choice of the concentration of the titration agent was based on a rapid potentiometric titration, which was

carried out to deduce the acid neutralising behaviour of the sample. The interval of pH-acquisition was set to 200 s (instead of 1 s) to give the system enough time to react and eventually neutralise the acid before more acid was added (Cappuyns et al., 2004a).
At regular time intervals (0, 0.5, 1, 3, 6, 12, 24, 48, 72 and 96 h), a sample of the suspension was taken over a filter (0.45 µm Acrodisc, Pall, East Hills, NY) by means of a syringe attached to a flexible tube (For more details see also Van Herreweghe et al., 2002). Immediately after sampling, the sample was acidified with a drop of concentrated $HNO_3$ (ultrapure) to bring the pH < 2. Subsequently the sample was kept in a refrigerator until analysis.

### *2.3 Analysis*

Analysis of Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn in the $pH_{stat}$ leachates was done by ICP-MS (HP 4500). The samples were diluted just before analysis with 5% $HNO_3$ (ultrapure). Standard series were made up starting from the '10ppm Multi-Element Calibration Standard-2A in 5% $HNO_3$' (Hewlett Packard, Palo Alto, CA). An Indium (In) internal standard was applied to both samples and standards. The spectroscopic interference of ArCl, which has the same m/z as As (75) was corrected according to the recommendations of the EPA (method 200.8, Brockhoff et al., 1999). Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below five percent. Accuracy was also checked by measuring standard solutions as unknown samples. In the final leachates, dissolved organic carbon (DOC) was measured with a TOC analyser (Skalar Formacs$^{HT}$ TOC analyser, Breda, The Netherlands); sulfate was measured by turbidimetry (Vogel, 1961) and chloride and phosphate by colorimetry (Jeffery, 1981). Electrical conductivity (18.34 EC-meter, Eijkelkamp, The Netherlands) and redox potential (Mettler Toledo Pt 4805-S7/165 Combination redox electrode, Zaventem, Belgium) were also determined. Geochemical modelling was performed with the thermodynamical speciation model MINTEQA2 4.02 (Allison et al., 1999).

### *2.4 Mathematical modelling*

ANC and leaching of metals as a function of time was described mathematically for both types of titration experiments by the use of MATLAB (The Mathworks, Natick, MA) and EXCELL (Microsoft, Redmond, WA) software.
ANC curves obtained in the $pH_{stat}$ tests with continuous setpoint titration were described according to Schwarz et al. (1999). The proton buffering capacity of soils during $pH_{stat}$ experiments can be described as the sum of two independent first-order reactions, i.e.:

$$H_b(t) = BC_1 (1- \exp(-k_1 t)) + BC_2 (1-\exp(-k_2 t)) \quad (1)$$

where $H_b(t)$ (mmol/kg) corresponds to the buffered protons at time $t$, $BC_i$ (mmol/kg) is the buffering capacity of system i, $k_i$ ($h^{-1}$) is the rate coefficient of the buffer system i and $t$ (h) is the time after starting the titration.
Analogously, the cumulative release of an element m at time $t$ is given by:

$$RL_m = RC_1(1- \exp(-r_1 t)) + RC_2(1- \exp(-r_2 t)) \quad (2)$$

With $RC_i$ (mg/kg) = the release capacity of buffer system i, $r_i$ ($h^{-1}$) is the rate coefficient of the buffer system i and $t$ is the time after starting the titration. The release capacities of the two buffer systems ($RC_1$ and $RC_2$) can be considered as two dominant sinks for heavy metals from which elements are released with a different rate. It has to be noticed that the two 'buffer systems' or 'pools' are only operationally

defined and that they are not automatically related to classical waste or sediment components. Theoretically, it is possible to consider more than two buffer systems, since the soils, sediments and waste materials consist of a variety of minerals which can dissolve upon titration. Additionally, metals can also be bound by inner- or outer-sphere complexes. To describe reaction mechanisms accurately, more complex models are commonly developed. As a consequence, apparent rate coefficients may be composed of several reactions, making it difficult to understand reaction mechanisms. It can be questioned whether the definition of more compartments would lead to a more comprehensive interpretation of the results of the leaching test. In the present work, two compartments, namely a 'labile' and a 'slowly labile' pool are considered. Besides the quantification of a 'labile' and 'slowly labile' pool of metals, each 'pool' is characterized by a release constant ($k_i$).

## 3 Results and discussion

### *3.1 Patterns of metal release as a function of time*

In general, 5 different types of heavy metal leaching behaviour as a function of time can be observed during $pH_{stat}$ leaching tests.

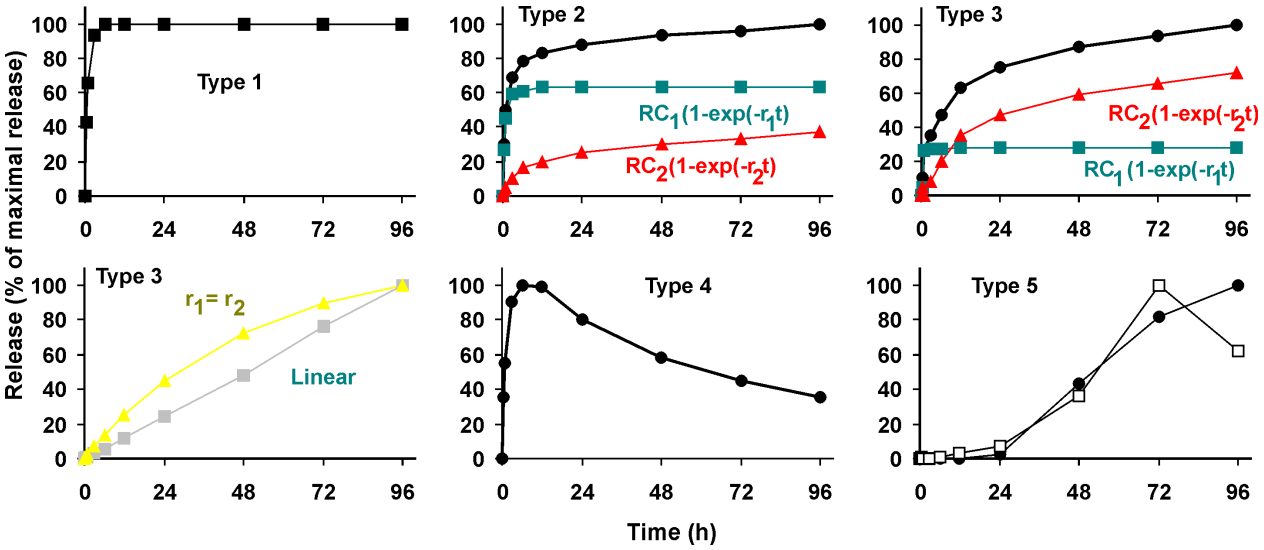


**Figure 2: Illustration of the different patterns of metal release observed during $pH_{stat}$ leaching tests and the mathematical description of metal release from 2 buffer systems or sinks ($RC_i$).**

- ***Type 1***: elements are rapidly released at the beginning of the experiment (e.g. Mg, Na, K); the 'labile' pool is by far dominant and likely related to cation exchange reactions
- ***Type 2***: some elements display an initially rapid release, followed by a slow but substantial release in the final stage of the experiment. The 'labile' pool is more important than the 'slowly labile' pool ($RC_1 > RC_2$ in equation 2). This pattern is typical for the more mobile metals in the soils (Cd, Zn, Ni) that are easily desorbed upon acidification or indicates the dissolution of poorly stable solid phases (e.g. carbonates)
- ***Type 3***: elements are released more slowly. In this case, the 'slowly labile' pool is more significant than the labile pool ($RC_1 < RC_2$ in equation 2). This release pattern points to the desorption of elements that are more strongly bound to soil constituents (e.g. Pb, Cr, Cu and Co) or to the slow dissolution of solid phases such as Fe-oxides. Sometimes, the release was linear as a function of time or could be described with only one exponential equation ($r_1 = r_2$ in equation 2).

- ***Type 4****:* some elements exhibit readsorption (As, P, which occur as anions in soil) or precipitation behaviour (e.g. Ba precipitates as $BaSO_4$).
- ***Type 5***: during combined oxidation and $pH_{stat}$ leaching of anoxic sediments, the release of metals often only starts after a certain period of time (between 6 and 48 h) (Cappuyns et al., 2004b, Cappuyns et al., 2005). This due to the slow oxidation kinetics of heavy metal sulphides.

### *3.2 Leaching as a function of pH*

Different patterns of leaching as a function of pH were observed during the $pH_{stat}$ test (Fig. 3). The leaching of Cd, Zn, Cu, Ni, Mn, Ca and Fe increased with decreasing pH, although a non negligible amount of these elements was also leached in the alkaline pH range, especially Cu, Ni and Fe. The solubility of Cd and Ni (relative to total concentration) as a function of pH is very similar for the different samples. In sample GB(fo), Zn is more soluble at high pH values than in samples GB(dr) and GB(cl); Cu is characterized by a lower solubility in the pH-range 2-6 in sample GB(fo).

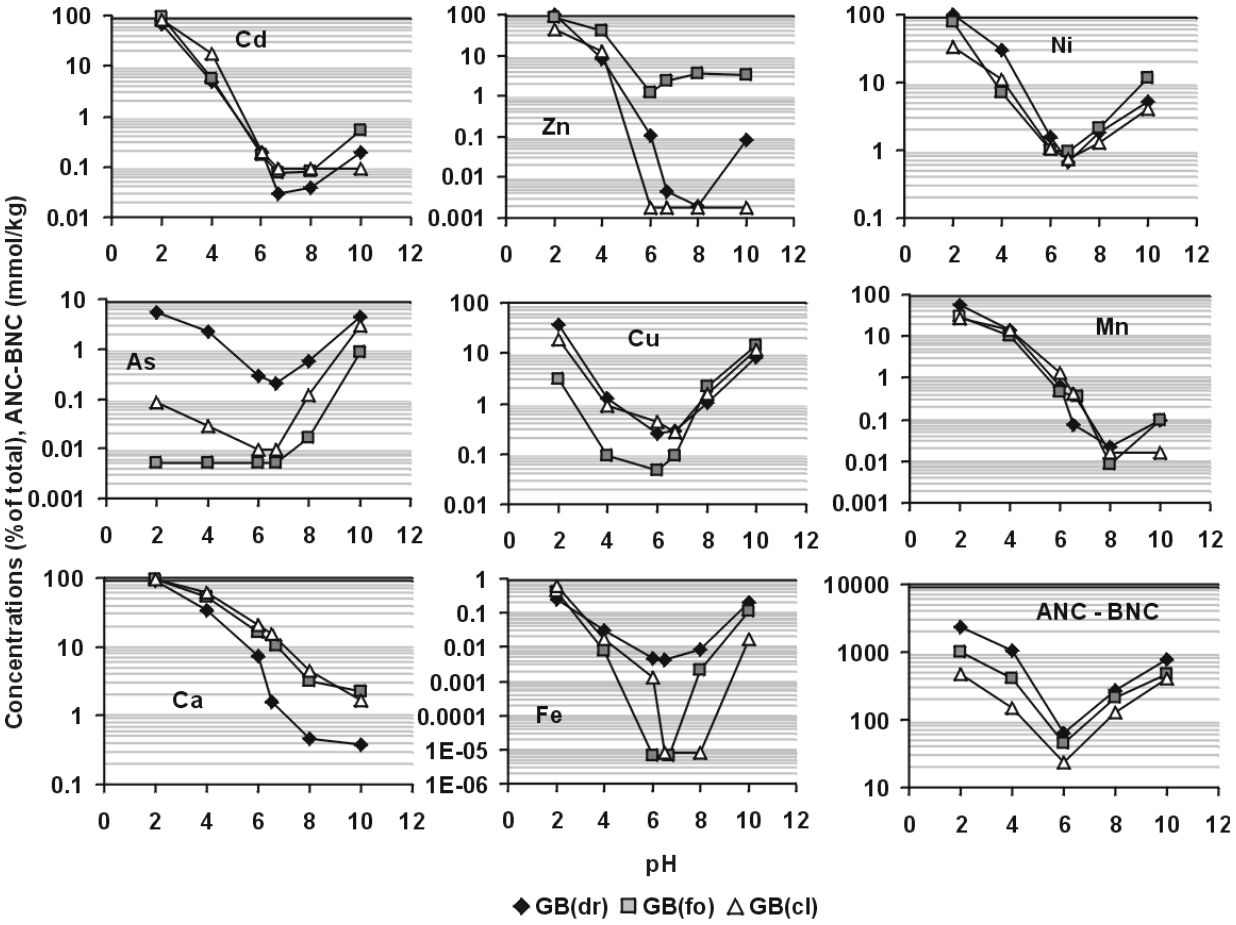


**Figure 3: Leached amount (% of total concentration) of Cd, Zn, Ni, As, Cu Mn, Ca, Fe and ANC-BNC as a function of pH during the $pH_{stat}$ test after 96 h in samples GB(dr), GB(fo) and GB(cl) (logaritmic scale).**

In soils and sediments, the solubility of heavy metals and As as a function of pH can usually be explained by the variation in surface charge as a function of pH. At pH values above the PZC, the sediment surface is negatively charged; pH values below the PZC result in a positively charged surface. This explains why cationic metals (e.g. Cd, Zn, Ni, Cu) are generally more soluble at low pH-values. However, complex formation with DOC can keep metals in solution at alkaline pH-values. Fe-(hydr)oxides have a $pH_{PZC}$ in

the range 6,3 – 9,1. The $pH_{PZC}$ of quartz is 2, but in sample GB(fo), quartz grains are coated with Fe-(hydr)oxides. Moreover, all the samples are characterised by an elevated organic carbon content, which tends to decrease the $pH_{PZC}$.

Since As occurs as arsenate in oxidized soils and sediments, a higher solubility is generally observed as pH increases. Nevertheless, the considerable solubility of As in the acid pH-range in sample GB(dr) (and GB(cl) to a lesser extent) (Fig. 3) cannot be explained by a variable surface charge as a function of pH. The increased solubility of As in sample GB(cl) at pH 2 is most likely due to the dissolution of clay minerals at low pH. Goldberg (2002) also observed a decreased sorption of arsenate on clay minerals (illite, montmorillonite and kaolinite) at pH-values below 4.

The solubility of DOC and anions (Fig. 4) generally increased with increasing pH, although $Cl^-$ was hardly influence by pH. The behaviour of $PO_4^{3-}$ and DOC was different in sample GB(dr), since a considerable leaching of $PO_4^{3-}$ and DOC was observed at low pH. The release of heavy metals from soils and sediments is to a large extent determined by the release of dissolved organic carbon. Organic carbon can bind metals and organic contaminants, whereas dissolved organic carbon can mobilise metals and organic contaminants.

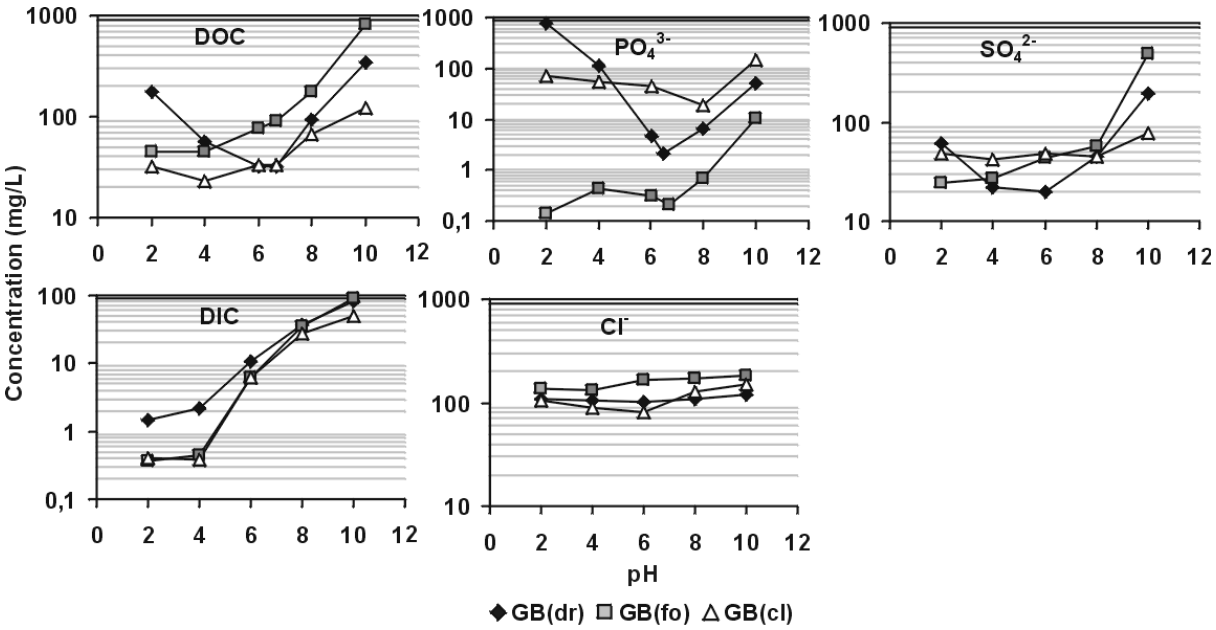


**Figure 4: Leached amount of DOC (dissolved organic carbon), DIC (dissolved inorganic carbon), $PO_4^{3-}$, $SO_4^{2-}$ and $Cl^-$ as a function of pH in samples GB(dr), GB(fo) and GB(cl) (logarithmic scale).**

### *3.3 Assessment of equilibrium conditions*

Leaching tests are generally based on two principles, i.e. equilibrium and diffusion controlled leaching. During leaching, the driving force is the concentration gradient between the porewater and the free water volume (Fälmann and Aurell, 1996). Chemical equilibrium is reached when there is no concentration gradient between the porewater and the free water volume. Batch and column tests are based on the assumption that chemical equilibrium is reached during the test. The mathematical description of leaching behaviour in $pH_{stat}$ leaching tests allows an estimation of equilibrium conditions, assuming that metal release during $pH_{stat}$ leaching will be at equilibrium at $t = \infty$. As a consequence, the reactive pool of an element released at a certain pH value is given by $RC = RC_1 + RC_2$ ($t = \infty$ in equation 2). In Fig. 5, the

release of Cd from the clayey sediment (GB(cl)) has reached more or less a plateau phase, suggesting equilibrium conditions.

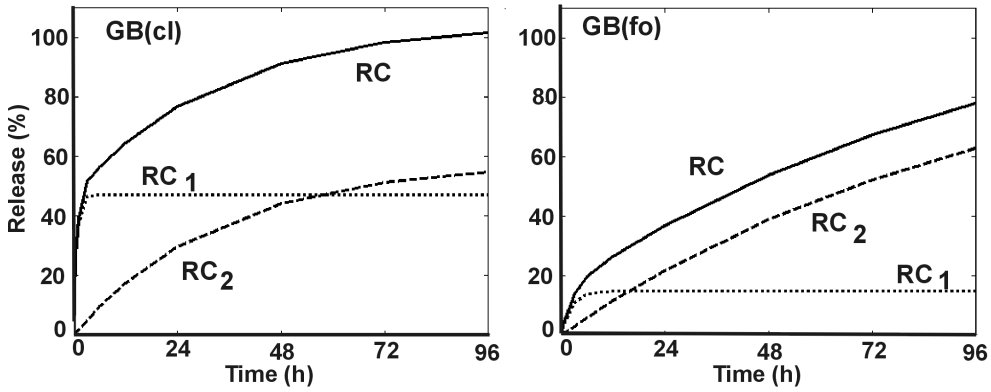


**Figure 5: Illustration of the kinetic fractionation of Cd at pH 4 into a 'labile' ($RC_1$) and 'slowly labile' ($RC_2$) pool according to Equation 2 in samples GB(cl) and GB(fo). The release of Cd is represented as % of the calculated maximal release.**

Consequently, the depletion of the reactive pool (= sum of 'labile' and 'slowly labile' pool) for Cd in sample GB(cl) is almost completed during the test. In sample GB(fo), however, leaching of Cd proceeds more slowly and equilibrium is not reached within the duration of the $pH_{stat}$ test, since only 85% of the 'labile' and 'slowly labile' Cd is released after 96 h (Fig. 5).

### *3.4 Combination with mineralogical analysis and thermodynamical modelling*

Based on the mineralogical composition of sample AN(t) (i.e. with minor amounts of troilite, arsenopyrite, willemite and magnesioferrite) and on the leaching of metals in this sample as a function of pH, geochemical modelling with MINTEQA2 was carried out. For Zn, it was assumed that all Zn released at pH 2 came from the dissolution of willemite. A good agreement was obtained between modelled and experimental release of Zn as a function of pH, indicating that the leaching of Zn could be explained by the dissolution of this zinc mineral (Figure 6A).

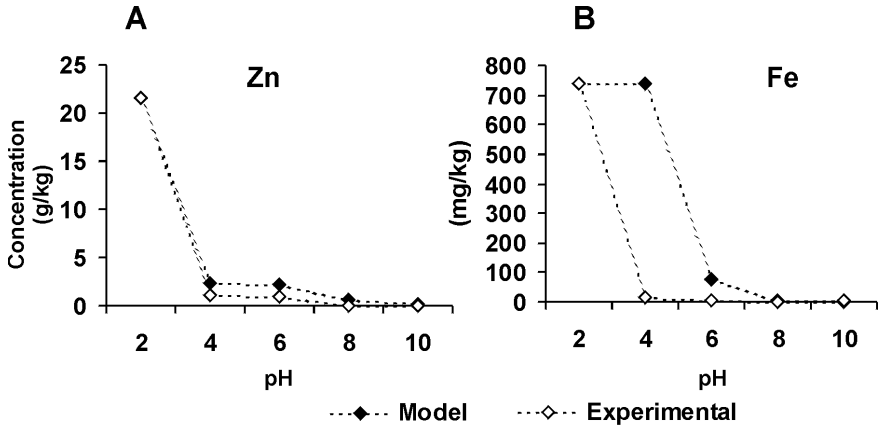


**Figure 6: Experimental and modeled solubility of (A) Zn and (B) Fe as a function of pH. The model is based on the assumption that willemite and triolite determine the solubility of respectively Zn and Fe respectively. See text for explanations.**

Slag dumps containing arsenopyrite should be chemically stable during long-term storage provided they are kept water-saturated and moderately reduced (Craw et al., 2003). Arsenopyrite decomposes in

oxidised waters. However, during $pH_{stat}$ leaching under oxic conditions (sieved < 2 mm fraction) almost no As was released in the pH range 2-8. This can be attributed to the occurrence of this mineral as minute phases occluded in glass phases, protecting the mineral from acid dissolution. The amount of Fe released during $pH_{stat}$ leaching was very low (600 mg/kg at pH 2, maximum 11 mg/kg at pH 4-11), suggesting that no significant dissolution of Fe-containing minerals occurs. Moreover, the dissolution of troilite (Figure 6B) and magnesioferrite as predicted by MINTEQA2, does not agree with the experimental results. Nevertheless, an important amount of Pb and Zn was released at pH 2 (respectively 77 and 70 % of their pseudo-total concentrations), indicating that the majority of Pb and Zn is not incorporated in troilite or magnesioferrite.

Based on the acid neutralizing capacity, heavy metal release upon acidification of the tailing material can be predicted. On medium long term (± 100 years) a rather limited release of Pb (± 4 mg/kg) has to be expected upon acidification. For Zn, however, more than 900 mg/kg could be released in a timespan of 100 years as a consequence of acid deposition.

## 4 Conclusions

- Based on $pH_{stat}$ leaching tests, an insight in heavy metal mobility in soils, sediments and waste materials as a function of pH is obtained and reactions occurring during acidification and alkanilisation are derived. Mathematical description of leaching behaviour as a function of time enables to distinguish between groups of elements with a different leaching behaviour, which can also be interpreted in terms of 'pools' of different reactivity. Additionally, $pH_{stat}$ titrations allow a determination of acid neutralizing capacity, making it possible to predict heavy metal release upon acidification, assuming a worst-case scenario.
- A multidisciplinary approach combining solid-phase chracterization (e.g. by X-ray diffraction, SEM-EDX) with chemical analysis and $pH_{stat}$ leaching tests can provide information on the composition of the waste materials and the reactivity of heavy metals in waste materials. Besides the solid phase characterisation of a material, the results of $pH_{stat}$ leaching tests can be supported by modelling predictions with thermodynamical codes (e.g. MINTEQA, PHREEQC).
- The European $pH_{stat}$ test, which is currently being standardized within the CEN framework (CEN-TC292/WG6,) consists of a 48 h $pH_{stat}$ test at 8 different pH-values in the range 4-12 (Hage and Mulder, 2004). Whereas, based on practical considerations, only the final leachate (after 48 h) is analysed, the analysis of the leachate at different time intervals is interesting because it allows to assess the kinetics of metal release. Additionally, the analysis of 'matrix elements', such as Fe and Ca, can provide information concerning the processes responsible for the release of contaminants.

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